

(12) UK Patent Application (19) GB (11) 2 276 392 (13) A

(43) Date of A Publication 28.09.1994

(21) Application No 9303546.7

(22) Date of Filing 22.02.1993

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(51) INT CL⁵
C11B 9/02

(52) UK CL (Edition M)
C5C CAA C107 C203
U1S S1339

(56) Documents Cited
US 4490398 A US 3828017 A

(58) Field of Search
UK CL (Edition M) A2B BSF2, C5C CAA CPB
INT CL⁵ A23L 1/221, C11B 1/10 9/02

(54) Fragrance Extraction

(57) A process for extracting fragrant, flavoursome or pharmacologically active components from natural materials comprises using non-chlorinated fluorinated hydrocarbon solvents. The process enables the more volatile components of plant derived materials, which are frequently lost in conventional methods of extraction, to be extracted. This results in the extracted components bearing a greater similarity to, and possessing a larger number of the characteristics of the original material than conventionally obtained extracts.

no co-solvent

GB 2 276 392 A

The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1990.

This print incorporates corrections made under Section 117(1) of the Patents Act 1977.

IMPROVED PRODUCTION OF NATURAL FLAVOURS & FRAGRANCES

This invention describes an improved means for the extraction, concentration and preservation of fragrances and flavours from natural materials.

Attempts to obtain and preserve those quintessential ingredients of natural products (both plant and animal) which are responsible for the expression of their characteristic aroma, fragrance and flavour have occupied the mind of man for many generations.

No process has yet been devised which ideally meets this need, though progress towards ever better techniques has accelerated in recent decades.

The ideal natural scent or flavour must aspire to the following criteria :-

- 1) It must be as highly concentrated as is possible.
- 2) Conversely, it must contain as little material which does not contribute to the aroma or flavour as is possible.
- 3) It must closely resemble the aroma or flavour of the original raw material, the more closely the better.
- 4) It must keep (have a 'shelf life' which is) as long as possible.
- 5) It should contain any nutritional, medicinal, pharmacological or beneficial properties possessed by the original raw material.
- 6) It must be economical in use.

Drying must have been the earliest attempt to preserve those desirable organoleptic characteristics of a natural product. Many culinary and medicinal herbs are highly seasonal and drying offers a way to preserve at least a small proportion of their fragrance and flavour for the winter in a slightly concentrated form, i.e. without water. To this day many people dry herbs and grind the dried material to powder for use in the enhancement of food flavour.

Seeds dry naturally, (e.g. pepper, cumin, coriander, cardamom,) and preserve flavour and aroma within them, which deteriorates only slowly. Nevertheless, this technique does not conform to our second criterion and efforts are made to extract and further concentrate the desirable characteristics of such seeds and dried products.

It has been realised since earliest recorded history, that flavours and aromas are (perhaps always) oil or fat soluble. Fragrant oils have been available since earliest times. They were used in ancient Egypt in the complex process of embalming. Homer tells us that Hector's body was anointed with aromatic oils after his death at the hands of Achilles at the battle of Troy (Illead).

Certainly the Romans prepared oil based scents and anointments, Stymmata was a liquid oily fragrance and Hedysmata was a solid unguent, probably based on lard mixed with natural resins.

Fragrant and flavoursome oils are a step nearer to the goal of preserved natural fragrances than dried materials, being more concentrated and less susceptible to deterioration.

One reason for the deterioration of concentrated fragrances over time is their volatility. It is of course, the transmission of the volatile scented molecules through the air from their source and into our noses, that allows us to perceive them as 'scents' and onto our palette as 'flavours'. Hence, loss of volatile components from a scented oil greatly reduces its quality.

As scents have become even more concentrated, it became apparent that 'pure' fragrances are, of themselves, volatile oils.

Attempts to obtain and entrap fragrant oils in an ever more original state have focused upon methods of extraction of the natural materials with a wide variety of organic solvents. It is an improved means of accomplishing this procedure which forms the subject of this specification.

The ideal 'solvent' for the extraction of fragrant oils and their preservation in their pristine state has probably not yet been exploited. One of the oldest techniques is that of 'enfleurage'. This process employed glass plates coated with purified lard which acted as a solvent for the fragrant oils of many flowers. The flowers were pressed into the lard and allowed to remain in contact with it for several days whilst their fragrant oils diffused and dissolved into the lard, which acted as a solvent. The exhausted flowers were removed and replaced with new ones, regularly throughout the harvesting season. At the end of the season, the lard, now saturated with fragrant oils, was scraped off the glass plates. It was referred to as 'pomade'.

This process takes account of the fragile nature of the aromas as

no heat is used. The pomade was never subjected to temperatures in excess of ambient and thermal decomposition and evaporation were reduced to a minimum.

Whilst excellent fragrances were preserved in the lard, the lard itself was a diluent and attempts were made to separate fragrant oil from it. This separation was accomplished by stirring the pomade with strong alcohol into which the fragrant oil preferentially dissolved. Gentle though it was, this procedure must have caused some spoilage of the flowers or scents, as the alcoholic solution containing the fragrance was itself later concentrated by removal of the alcohol from the oil. This process was exceedingly labour intensive and hence very expensive. It is probably no longer practised, but for hundreds of years, it was the only means available for the preparation of high quality jasmine and tuberose oils.

The technique of 'maceration' was developed as an attempt to accelerate and therefore reduce the cost of enfleurage. In this procedure, vats of molten lard were stirred with fresh flowers. The fragrant oils from the flowers dissolved in the molten lard, which was filtered from time to time in order to remove 'spent' flowers allowing their replacement with new ones. At the end of the season, the molten lard was mixed with alcohol which dissolved the fragrant oils from the insoluble lard and permitted their separation from it as solutions in alcohol. This technique was quicker and cheaper than enfleurage but inevitably, the fragrant oils obtained were of poorer quality due to thermal decomposition of the fragrances and loss to the atmosphere of their most precious and most volatile 'notes' resulting from the elevated temperature.

The alcoholic treatment, which was still required, ensured a further deterioration of the final fragrances, it being necessary to remove the alcohol from the alcoholic solution in order to leave the purified fragrant oil or 'absolute' in its final useable form.

Lard was not an ideal solvent for floral fragrances, as it required a great deal of purification before being used and inevitably deteriorated, becoming oxidised and somewhat rancid during long use. Vegetable oils would have been more convenient (being liquid fats at room temperature) but because of their higher degrees of unsaturation, they would have become rancid even more quickly.

As they have become more readily available, those organic solvents which are volatile liquids at room temperature offered obvious advantages. Not only was it easier to separate their solutions from the extracted flowers once dissolution of the fragrant flower oils has occurred, but they may be easily evaporated in the interests of concentrating the solute, leaving a concentrated residue (or 'concrete' behind). Regrettably, the boiling point of the most popular solvents is higher than that of those precious light, volatile notes of the fragrance or flavour which are the very components so valued by the end-user. Furthermore, the heating of the solution to its boiling point (60°C in the case of hexane) contributes to a further reduction in quality as a result of thermal degradation.

Vacuum distillation can reduce the degree of thermal decomposition by reducing the boiling point of the solvent, nevertheless it does nothing to alleviate the 'stripping' of the volatile notes into the vapour phase whilst under reduced pressure.

The ideal solution to these problems, would be a solvent with a boiling point substantially lower than that of the most volatile component of the fragrance. Even more ideally the solvent should be selective in as much as it is able to dissolve only the pure fragrant oils (absolutes) leaving as many undesirable components behind as possible. Apart from the spent flowers themselves, these 'impurities' are mainly waxes. Such 'selectivity' would eliminate the need for further alcoholic treatment of the extract, saving considerable expense and eliminating any chance of further deterioration of the fragrance quality.

Such solvents have been found.

Gaseous carbon dioxide at temperatures in excess of 39°C (its critical temperature) has been found to be an excellent solvent for fragrant oils at pressures in the region of 350 BAR (5000 psi). Passing such a fluid through tubes packed with fragrant or flavoursome materials strips the fragrance or flavour from the raw material into the fluid stream. Allowing the pressure of the gas thereafter to fall to 100 BAR or less, deprives it of its ability to dissolve these oils and they precipitate from the fluid stream and can be collected. The low pressure carbon dioxide may then be re-compressed and recycled or simply discarded.

This apparently 'ideal' solution to the problem is enhanced further, as a result of the finding that the pressure of the carbon dioxide gas during the extraction of the fragrances or flavours can, to some extent, affect the exact nature of the components extracted. This solvent is therefore somewhat selective. Low pressure CO₂ (200 BAR) selectively extracts more volatile

materials, in lower yields, than high pressure CO₂ (350 - 500 BAR) which extracts the remaining less volatile materials, in higher yield.

Were it not for the cost of the capital equipment, such 'super-critical CO₂' extraction procedures would be the ideal means for the extraction of flavours and fragrances from all manner of natural raw materials.

Unfortunately and inevitably, the capital cost of such high pressure processing equipment is very great indeed. So great in fact that it is completely uneconomic to use this process for the production of fragrances from raw materials such as fresh flowers or herbage.

For 'dry' materials (such as those with a water content of less than 30%) wherein the oils constitute more than 10% of the dry weight, this process is undoubtedly the best technique for the extraction of flavours and fragrances, available today. Such dry materials are of commercial significance. Coriander seeds, cumin seeds, celery seeds, dried roots, bark, wood and artificially or naturally dried herbage (such as hops which are pelletised to increase their bulk density) are excellent candidates for super critical CO₂ extraction yielding fragrant oils or flavours of unsurpassable quality.

Fresh flowers or herbage, on the other hand, frequently contain water to in excess of 90% of their fresh weight. The total yield of fragrant oils contained in such wet, fresh flowers is frequently as low as 0.1% These characteristics render such raw material

entirely unsuitable for extraction using super critical CO₂, on the grounds of cost.

Unfortunately, as has been pointed out above, drying of fragrant crops such as flowers which might have been expected to increase their bulk density, can cause serious loss of volatile characteristics thereby obviating, in large measure, the advantages of the CO₂ process. Hence drying is no answer to this dilemma. Furthermore, super critical CO₂ extraction systems must operate at temperatures in excess of 40°C. Holding labile fresh natural materials at such temperatures for long periods during processing may well result in thermally or enzymically induced spoilage and the development of 'off' aromas and flavours.

Furthermore, during extraction of aromas or flavours with high pressure CO₂, the pH of the aqueous phase of such wet, fresh flowers declines to very low values. It is well known that carbon dioxide dissolves in water with a depression of its pH and that this depression is broadly proportional to the pressure of the CO₂ in contact with the water. The effect of such low pH on the quality of the final extract might be to damage the aroma obtained.

Though other 'gases' have been assessed for their ability to extract fragrant oils from fresh plant material, the only one which had previously been brought to commercial realisation was butane. Butane has a boiling point of -0.5°C at atmospheric pressure and therefore has conspicuous advantages over solvents such as hexane (boiling point +60°C) when its removal from a solution of fragrant oils is undertaken. Its removal causes less loss of the light, fragrant components than does the removal of hexane.

Were it not for the extreme flammability of this class of (hydrocarbon) gases, presumably propane, ethane and methane would be expected to be even more desirable solvents having lower boiling points than butane. Though hexane is flammable, of course, it has a relatively low vapour pressure at ambient temperatures, whereas all the other hydrocarbon gases (having substantial vapour pressures at room temperature in liquid form) must be manipulated in sealed, pressure vessels and equipment.

The flammability of liquified hydrocarbon gases, under pressure renders their routine handling by process plant operators, extremely hazardous. Leakage of even minute quantities of these heavy odourless flammable gases constitutes a potential risk of incineration to the operators and their equipment, of unimaginable horror.

Of the solvents which might be substituted for liquified hydrocarbon gases, one candidate would be dichloro difluoro methane (a CFC or chloro fluouro carbon). Indeed this material has been used in experimental extraction processes with a considerable degree of success and 'concretes' of very high quality have been easily obtained. However, since the realisation of the effects of such CFC's on the ozone layer of the earth's atmosphere, not only has legislation been enacted to phase out the use of such solvents, but public opinion would be unlikely to favour the use of fragrances or flavours derived by such means.

Our approach to the development of a practicable inexpensive means of producing high quality flavours and fragrant oils from plant materials has lead us to employ the solvent tetra fluouro ethane

(T.F.E.).

This material has been developed as a replacement for the chloro fluouro carbon dichloro-difluoro-methane, used throughout in the refrigeration industry, with one which is 'ozone' friendly.

TFE is not flammable. It has a boiling point of -26°C at atmospheric pressure.

Though it must be admitted that this material is a 'greenhouse' gas, its effect on global warming is only slightly more than that of carbon dioxide.

The vapour pressure of this solvent at room temperature (20°C) is 5.6 BAR. Hence though it must be handled in equipment which is capable of tolerating such pressures, this equipment is a fraction of the cost of equivalent equipment required for the handling of for example super critical CO_2 and a fraction of the degree of sophistication or hazard inherent in plant for handling hydrocarbons gases under pressure.

By carefully designing such process plant, the solvent may be recovered from the extraction process and from solutions of fragrant oils wherein it is the solvent, to very high levels of efficiency. Good environmental practice demands that equipment using this solvent should be capable of recovering it so that losses of solvent from the process are kept to a minimum. This is also necessary on the grounds of cost. Current prices for this solvent are extremely high, but are widely predicted to fall as use of this material in commercial refrigeration equipment becomes

universal and mandatory.

For the economical extraction of high quality fragrant oils and flavours from fresh flowers and herbage, this solvent would seem to be difficult to improve upon.

A review of its advantages shows that it is :- not flammable, of low boiling point (considerably lower than butane), not offensive to the general public from the environmental standpoint, of very low toxicity, easily handled in inexpensive equipment, readily available in Europe and likely to become readily available in the rest of the world, though its cost is currently high, it is very likely to decline significantly as its use in refrigeration systems becomes more widespread. It might have been expected to yield very high quality fragrant concretes. However, its primary and most spectacular advantage, which could not have been anticipated by those versed in the art, is its ability to directly and selectively extract mobile liquid flavours and fragrant oils and not solid waxy concretes. We have found that this solvent leaves behind the majority of the waxes and other non-fragrant materials normally extracted with solvents.

The products of the extraction of fragrant flowers and herbs using this solvent are clear mobile liquids at ambient temperatures (20°C). These liquids contain only small amounts of low molecular weight waxes and hence, may be employed by perfumers directly without further alcohol treatment.

The advantages of this will be obvious to practitioners of the art.

Hitherto, the primary products available from solvent extraction processes (which have previously been referred to as 'pomade' or 'concrete') have not been directly useable by the perfumer. Concrete contains not only the fragrant oils required, but also natural waxes with a wide diversity of molecular weights. Waxes being esters of fatty acids and fatty alcohols and 'pomades' contain lard.

Most 'concretes' are waxy semi solid masses, from which 'absolute' fragrant oils must be carefully extracted or separated by means of trituration with alcohol, as has been described earlier. In order to rid the alcohol of residual dissolved waxes, it has been necessary to chill these alcoholic extracts to temperatures as low as -25°C to precipitate the waxes and filter them.

Having obtained the filtrate or solution of fragrant oil (or 'absolute') in alcohol, it is then necessary to remove the alcohol from the 'absolute'.

This has been accomplished normally by distillation, often at reduced pressure. Shaking of the alcoholic solution with aqueous solutions of salts, usually sodium chloride, in which the alcohol preferentially dissolves has also been found to leave the fragrant oil or absolute as a layer floating on its surface.

It has already been stressed that such treatments of fragrant oils, however carefully carried out, inevitably result in loss of quality of the fragrant oils produced.

Furthermore, the presence of ethyl alcohol in products at any

concentration causes great offence to customers who are devout Muslims. Hence, the extent to which it is necessary to go to rid 'absolute' fragrant oils of their final traces of ethyl alcohol, need to be very rigorous indeed and cause severe damage to the final absolute flavour or fragrance.

The use of tetra fluouro ethane however obviates this complication totally. No alcohol whatsoever is needed in order to render the products of extraction of fragrant flowers directly useable by the perfumer as fully finished flavour or fragrant oils.

EXAMPLE A

50kg of freshly picked Rosa Damascena Trigintipetala were introduced into a stainless steel extractor fashioned in the shape of a flanged tube 180 litres in capacity furnished with removable end caps, each of which comprised a plate upon which a sheet of stainless steel mesh of 200 micron pore size had been secured by way of a filter. The end caps or plates were also equipped with a port with was capable of closure and through which both gases and liquids could pass via the 200 micron stainless steel filter mesh.

The extractor was closed and air was pumped out to a pressure of less than 10 mbar absolute. (28" Hg vacuum or more).

A source of supply of liquid tetra fluoro-ethane was connected to the extractor and liquid solvent was allowed to pass to the extractor. The contents of the extractor were bathed in 67kg (50l) of tetra fluoro ethane.

The extractor was sealed and the source of TFE was disconnected. The extractor was then tumbled on its lateral axis for two hours to ensure intimate contact between the solvent and the roses.

After two hours, the tumbling was stopped and the outlet, now vertically inclined, was connected via alternative pipework, to a small evaporator of 50 litres capacity which had itself previously been ^{vacu}evacuated to 10 mbar absolute vacuum. The solution of rose oil in the TFE solvent was allowed to pass intermittently from the extractor into the evaporator, to retain a level of liquid and a gas filled headspace in the evaporator. The evaporator was then connected to the inlet of a compressor which was allowed to withdraw TFE gas from the head space of the evaporator and compress this (on its outlet side) to 5 bar. ✓

At a pressure of 5 bar, and cooled to room temperature, the gas re-liquified and could either be recycled to the extractor to flush out residual rose oil or be re-introduced to the original reservoir of solvent for re-use on a further batch of fresh flowers.

Inevitably, during this process, the 'evaporator' cooled to very low temperatures and it was desirable to immerse it in a water bath furnished with an immersion heater and thermostat. The thermostat was set to activate the immersion heater when the water temperature fell to 10°C and to switch off the heater whenever the temperature of the water exceeded 12°C.

The pressure contained in the evaporator throughout this process was in the region of 30 psi.

As soon as all the solution from the extractor had passed to the evaporator, and all the solvent from both the extractor and evaporator had been evaporated, the vapour pressure inside the evaporator began to fall.

When this pressure had fallen to 0 psig an outlet on the bottom of the evaporator was opened and the rose oil solute was allowed to run into a suitable receptacle. | ✓

Weighing of the receptacle before and after the introduction of the rose oil revealed that 50gms of rose oil had been removed from the extractor (a yield of 0.1%).

The rose oil so obtained was a clear, mobile amber liquid with an excellent aroma characteristic of roses.

Following the removal of the rose oil, the compressor was allowed to continue to suck residual solvent vapour from the extractor and the roses within it. By the time the pressure within the extractor had fallen to 10mbar (28"Hg vacuum), over 99.9% of the TFE solvent had been returned to the original reservoir.

However, in order to improve the recovery of solvent from 99.9% to 99.99% it has been found necessary to introduce heat to the extractor and its contents which would otherwise decline in temperature and hence reduce the vapour pressure of the solvent at the input to the compressor thereby starving it and reducing its efficiency.

EXAMPLE B

Some 2400 brown dried vanilla pods were frozen and roughly chopped into pieces approximately 2mm³.

The weight of chopped vanilla pods after thawing was 6500 gms.

This material was introduced into the extractor and 20 litres of TFE were brought into contact with it (following the removal of air).

After tumbling as in the previous example, the solution was allowed into the evaporator and the solvent removed exactly as described previously.

Three identical extractions using 20 litres of fresh solvent in each case yielded a pale yellow clear oil of characteristically vanilla aroma and flavour in a total quantity of 450 gms. A yield of 7% or thereabouts.

CLAIMS:

1. A process for extracting one or more components from material of natural origin, the process comprising the steps of:
 - 5 a) contacting the material with a non-chlorinated fluorinated hydrocarbon solvent in the liquid phase so as to charge the solvent with the component,
 - b) collecting the charged solvent, and
 - 10 c) removing the solvent to isolate the component.
2. A process as claimed in claim 1, wherein the material is contacted with the solvent in an extraction vessel after the vessel has been sealed and air has
 - 15 been removed, and wherein the mixture of the solvent and the material is maintained under pressure so that the material and the solvent are in intimate contact and the solvent is charged with the component.
3. A process as claimed in claim 1 or 2 wherein the
 - 20 temperature of the solvent is not more than 40°C when in contact with the material.
4. A process as claimed in claim 3 wherein the temperature of the solvent is not more than ambient temperature.
- 25 5. A process as claimed in claim 1, 2, 3 or 4 wherein the solvent is one or more of: CF_3H , CH_3F , CH_2F_2 , $\text{CF}_3\text{CF}_2\text{H}$, CF_3CH_3 , HCF_2CH_3 , $\text{CF}_3\text{CHFCH}_3$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$, $\text{CF}_3\text{CH}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{F}$, $\text{HCF}_2\text{CF}_2\text{CF}_2\text{H}$ and $\text{CF}_3\text{CHFCH}_2\text{F}$.
- 30 6. A process as claimed in any of claims 1 to 5 wherein the solvent is 1,1,1,2-tetrafluoroethane. ✓
7. A process as claimed in any preceding claim wherein the material of natural origin is selected from: flowers, bulbs, corms, moulds, yeasts, fungi,
 - 35 algae, lichens, herbs, seeds, bark and buds.
8. A process as claimed in any of claims 2 to 7

wherein the pressure in the extraction vessel is not more than 40mbar after the air has been removed and before the solvent has been introduced.

9. A process as claimed in any of claims 1 to 8
5 wherein the material is contacted with the solvent in an extractor, and wherein the extractor communicates with a source of the solvent to supply solvent to the extractor and with an evaporator to remove the solvent from the charged solvent in order to isolate the
10 component.
10. A process as claimed in claim 9 wherein the evaporator communicates with a compressor which supplies liquefied solvent to the solvent source and/or the extractor.
- 15 11. A process as claimed in claim 9 or 10 wherein the evaporator includes a source of heat for controlling the temperature of the evaporator.
12. A process as claimed in claim 11 wherein the source of heat is thermostatically controlled to
20 maintain the temperature of the evaporator.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(the Search report)

Application number
GB 9303546.7

Relevant Technical Fields

(i) UK Cl (Ed.M) C5C (CAA; CPB) A2B (B5F2)

(ii) Int Cl (Ed.5) C11B 1/10; 9/02; A23L 1/221

Search Examiner
K J KENNETT

Date of completion of Search
28 JUNE 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii)

Documents considered relevant following a search in respect of Claims :-
1-12

Categories of documents

X: Document indicating lack of novelty or of inventive step.

P: Document published on or after the declared priority date but before the filing date of the present application.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

A: Document indicating technological background and/or state of the art.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	US 4490398 (BEHR) column 2 line 32	1-5, 7, 9, 10
X	US 3828017 (FINLEY) whole document	1,3,4,5,7

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).